Hydrodynamic effects in superparamagnetic particle aggregation processes

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Abstract: The goal of this work is to study and understand the aggregation dynamics of superparamagnetic particles in a viscous medium and evaluate the effect of hydrodynamic interactions through molecular dynamics simulations. We will compare the system behaviour taking hydrodynamic effects into account in front of the case where they are not considered. Finally, we will also study the response of the system when introducing a Couette flow.

I. INTRODUCTION

We investigate the aggregation behaviour in superparamagnetic particles of micrometric scale in a viscous fluid when applying an external magnetic field.

The study of superparamagnetic materials is important as they have very diverse applications, usually used in the form of a colloid. In other words, the system is composed of two different phases: one is the magnetic particles and the other is the continuous fluid. For this reason it is important to study the hydrodynamic effects generated by the viscous medium on the particles. Examples of applications can be ferrofluids that are used as lubricants or sealants, multifunctional materials such as reconfigurable coatings and materials for biomedical applications like immunoassays, drug delivery or hyperthermia treatments. Understanding the behaviour of this particles can also be useful to separate particles of different sizes by applying a certain type of flow in the fluid.

The problem consists of investigating the dynamics of a system of N superparamagnetic particles in a magnetic field initially distributed randomly in a L edge box where the particles interact with each other in different ways (magnetic, steric and hydrodynamic interactions). To see the evolution of the particles we will use molecular dynamics simulations. These simulations consider the forces on a particle due to all the other particles of the system and use an iterative algorithm to obtain the evolution in time of the position and velocity of the particles.

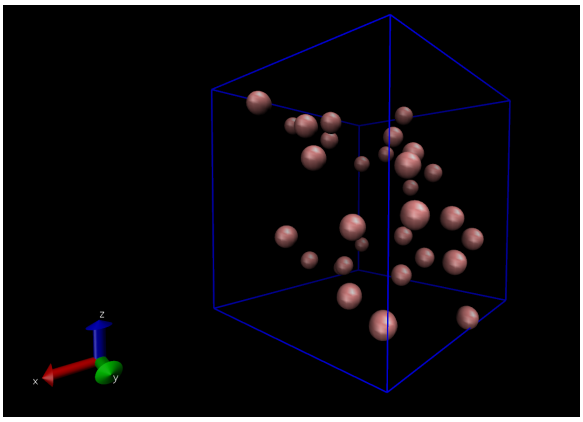

FIG. 1: Snapshot of the initial system distribution. Particles occupying the box in random positions.

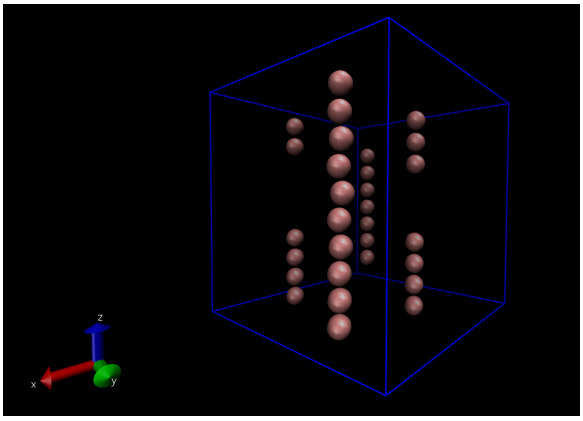

FIG. 2: Snapshot of the final system distribution. Particles assembling into chains in the $\hat{z}$ direction.

II. INTERACTION FORCES

The physical form of the system consists of independent particles inside a box filled with a viscous fluid. Now we will explain the different interactions we have taken into account when calculating the total force applied to each of these particles.

A. Periodic boundary conditions and cutoff

First of all we have taken into account a *cutoff* that makes the force equals to zero if the distance between particles is greater than a certain value. We can do that, because all the interactions that we will contemplate decrease rapidly with distance and therefore, we can suppose that after the cutoff distance they are small enough to neglect them. The purpose of doing that is to give the same importance to particles that are at the same distance, a fact that would not happen when applying periodic boundary conditions in a square box.

The periodic boundary conditions are such that if a

particle comes out of the box on one side, enters on the opposite side with the same speed. We can imagine this conduct as if the particle enters a box identical to ours but adjacent. Related to the periodic boundary conditions we also have to explain that the force applied to each particle comes from the procedure called the method of images, where we have only considered the first images. So if the image of particle is closer than the particle itself, it will be the position of this image that we will consider when calculating the force.

B. Dipole-dipole forces

When applying a magnetic field $\vec{B}$, paramagnetic particles acquire a magnetic dipolar moment.

$$\vec{m} = \chi \vec{B} \tag{1}$$

Where $\vec{m}$ is the dipolar moment and χ is the magnetic susceptibility.

The force between two dipoles is given by,

$$F = \frac{3\mu_0}{4\pi|r|^5}\Big[(r \times m_1) \times m_2 + (r \times m_2) \times m_1 - 2r(m_1 \cdot m_2) + 5r\frac{((r \times m_1) \cdot (r \times m_2))}{r^2}\Big] \tag{2}$$

Where μ_0 is the permeability of vacuum, r is the distance that separate two particles and m_1 and m_2 are the dipolar moments of each particle.[1]

Since the magnetic field that we apply is oriented in the direction of the axis $\hat{z}$, we can assume that magnetic moment will be oriented in this direction too, see Eq. (1).

We consider large enough particles such that magnetic contributions are much greater than the thermal ones allowing us to disregard the last ones, which simplifies the description of the system a lot since we have eliminated the dependence with the temperature.[2]

C. Repulsion forces

Actual particles can not overlap because they occupy a certain volume, so we must apply a force between them that does not allow two particles to be closer than a certain distance. This force is created by a modification of the Lennard-Jones potential,

$$V(r) = \begin{cases} 4\epsilon\Big[\Big(\frac{\sigma}{r}\Big)^{12} - \Big(\frac{\sigma}{r}\Big)^{6}\Big] & if \quad r < r_{max} \\ 0 & if \quad r > r_{max} \end{cases} \tag{3}$$

where ϵ is the depth of the potential and σ is the distance where the potential is zero (the repulsion contribution and the attractive one have the same value).

In our particular case we have imposed $r_{max} = 2^{1/6}\sigma$ (this value of r is where we find the minimum potential). Thus, this potential only introduces repulsive forces between particles.

D. Hydrodynamic forces

Now we can consider the fluid effect on the motion of the particles. Under these circumstances two effects will take place.

- The fluid will be able to generate friction on the particles causing a force that opposes movement,

  $$F = 6\pi\eta R v \tag{4}$$

  Where v is the speed of the fluid, R is the particle radius and η is the viscosity of the fluid.[3]

- Hydrodynamic interactions between the particles as a result of the fluid presence. The movement of a particle disturbs the fluid around it and this affects the other particles.

The flow of a fluid is described by the Navier-Stokes equation which turns out to be nonlinear with the velocity of the fluid, but for cases with a Reynolds number small enough ($Re << 1$)[4], we can scorn a part of the equation and convert it into one that has a linear behaviour. The Reynolds number is described by the following relation between magnitudes:

$$Re = \frac{forces\ due\ to\ inertia}{forces\ due\ to\ friction} = \frac{\rho v a}{\mu} \tag{5}$$

Where ρ is the fluid density, a is the typical linear distance of the system and μ is the dynamic viscosity, a constant of the system.

Therefore, for small Reynolds the system will be dominated by friction, and inertia will not play an important role. This approach is valid in our case since the *Re* numbers are the order of $10^{-4} - 10^{-5}$. In these conditions the terminal velocity of the particle in the fluid is reached immediately and therefore the velocity is proportional to the force, where the constant of proportionality is a matrix called mobility tensor μ (which can be of four different types, translational-translational, translational-rotational, rotational-translational and rotational-rotational coupling). If we take into consideration all the contributions of all the particles acting on all the others, we can write in a general way $V = M \cdot F$, where V is a vector with the linear and angular velocities of the particles, F is a vector with the forces and torques of the particles and M is known as the mobility matrix that is a generalization of μ.

It is necessary to mention that we have approximated the particles as punctual when dealing with the hydrodynamic effects. Assuming small Reynolds numbers, the Navier-Stokes reduces to the so called *creeping flow equations*[4],

$$\begin{aligned} \nabla p(r,t) - \mu\nabla^2 u(r,t) &= f_{ext}(r) \\ \nabla \cdot u(r,t) &= 0 \end{aligned} \tag{6}$$

Since these are linear equations, the solution for a punctual particle is given by the relation $u(r) = T(r - r') \cdot F_0$

where T is the Oseen tensor and u the fluid velocity. This gives us the relation between the velocity of the fluid at point r due to a force at point r'. This tensor has a simple form for the case of punctual particles[4],

$$T(r) = \frac{1}{8\pi\eta}\left(\frac{1}{r}\hat{\mathbf{I}} + \frac{\mathbf{rr}}{r^3}\right) \tag{7}$$

Where $\hat{\mathbf{I}}$ is the identity matrix.

Finally, another configuration we have studied is the case where the system box has a wall at the plane Z=0 causing that the particles can not go below this point and they can go as high as wanted. To satisfy no-slip boundary conditions, the interaction between particles taking into account the existence of the wall is given by the Blake tensor, a large tensor that includes the Oseen one and adds the hydrodynamic effects of the wall upon the fluid based on the image method.

III. MOLECULAR DYNAMICS

In view of the fact that the systems to study do not have an analytical solution, we use numerical methods to solve the equations of the movement. Molecular dynamics consists in simulating computationally the movement of particles given the whole interactions between them.

The Verlet algorithm resolves the equation $f_i = m_i\ddot{r}_i$ to second order and reversibly over time. We have adopted the so called Velocity Verlet algorithm [5], to build the simulations of our problem. In this variant of Verlet's method, we need to compute the velocity of the particle to calculate the position, fact that allows us to have an expression of the speed, an important thing for hydrodynamics.

The algorithm works in the following way; given the positions and speeds at time t, we determine the forces that act on the particles and the algorithm figures out the positions at time $t + \delta t$. It is worth remembering that if we know each force it is the same that knowing each acceleration through Newton's equation.

$$r(t + \delta t) = r(t) + v(t)\delta t + \frac{1}{2}a(t)\delta t^2 \tag{8}$$

Then we calculate the forces at time $t + \delta t$ using the positions at this moment of time so we can find the speed in the following way,

$$v(t + \delta t) = v(t) + \frac{1}{2}\delta t[a(t) + a(t + \delta t)] \tag{9}$$

IV. SIMULATIONS AND RESULTS

The magnitude of the values with which we work is very small in the International System of Units. Therefore, to optimize the simulations and not require so much memory space for the storage of those magnitudes, we have made a change of units to units that we have called system units. These units are such that the new unit of distance is the particle radius, the new unit of mas is the particle mas and the new unit of time is the time that satisfies that the viscosity equals one.

Magnitude	**International System**	**System Units**
Particle radius	10^{-6} (m)	1.00
Particle mass	$8.377600 \cdot 10^{-15}$ (kg)	1.00
Viscosity	10^{-3} $(\frac{kg}{m \cdot s})$	1.00
Time	$8.3776 \cdot 10^{-6}$ (s)	1.00
Magnetic field	0.10 (T)	0.10
Particle susceptibility	$6.666667 \cdot 10^{-13}$ $(\frac{J}{T^2})$	$5.585067 \cdot 10^{3}$
Vacuum permeability	$4\pi \cdot 10^{-7}$ $(\frac{T^2 m^3}{J})$	$1.5 \cdot 10^{-4}$

TABLE I: Values and units of the quantities used in the system simulation.

Now that we have introduced the values to characterize the particles, the fluid and the different interactions described in the previous section, we need to place the particles into our volume. To do this, we made a small program that place the particles inside the box of our system randomly.

Once this is done, it is necessary to introduce the time steps that we want to simulate and we can start the computation process. In each time step, all the forces on each particle described above are calculated and through the Velocity Verlet algorithm we calculate the positions and velocities of all of them.

Then with a program named VMD (Visual Molecular Dynamics), which is a program of molecular modelling and visualization of structures, we have been able to observe the evolution of our system.

For the analysis of the results we have made a program, written in Python, able to read the system dimensions and the positions of the particles in each time step. Given a minimum distance of approach between them below which we consider those particles linked, the program counts the number of chains formed and their average length taking into account periodic boundary conditions.

A. Simulations without hydrodynamic interactions

First we have imposed that inside our simulation box there are no hydrodynamic interactions, meaning that the only forces that are applied to the particles are the magnetic forces, the repulsion ones and friction with the fluid. We can see that the particles are grouped, and after a while we can observe chains in the direction of the magnetic field.

If we simulate systems with different numbers of particles in the same volume, which is the same as changing the density of the system, we can see that after the same number of time steps, the chains of systems with smaller densities have a smaller average length, see FIG (3). The cause of this effect is that having more density of particles, implies that they are closer to each other and it

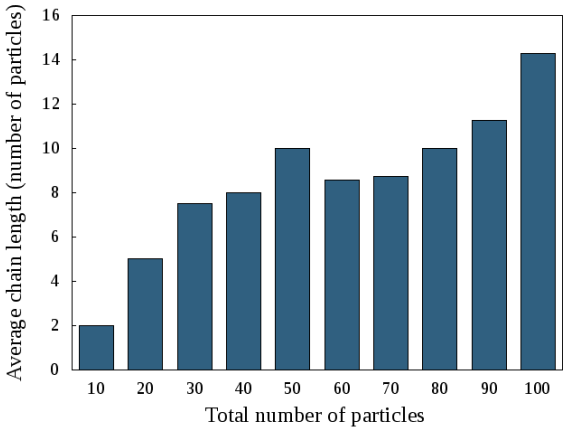

FIG. 3: Histogram showing the average length of the chains after 200 million time steps for different values of the number of particles in a box whose edges measures 20 (system units).

does not take that long for the magnetic force to piece together two of them. It is necessary to emphasize the fact that the particles are placed randomly so the distance between them is arbitrary, it would be possible for a system with less density to have its particles closer to each other than a system with a larger density.

B. Simulations with hydrodynamic interactions

In this section we assume that within our box we have a fluid and therefore the particles will suffer the hydrodynamic interactions implemented with the Oseen tensor. Taking this into account we see that chains are also formed so we are going to compare the evolution of these chains with hydrodynamic interactions and without them.

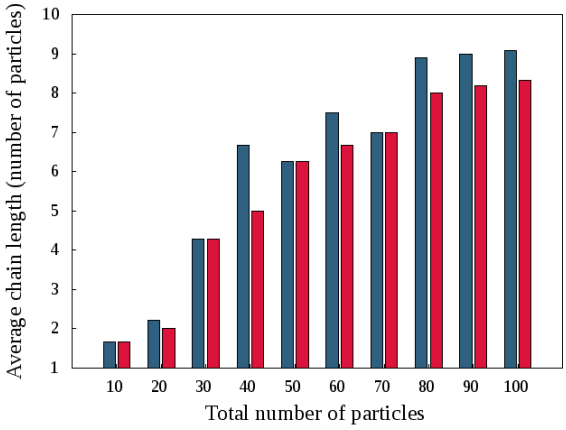

FIG. 4: Histogram showing the average length of the chains after 60 million time steps for different values of the number of particles in a box whose edges measures 20 (system units). Blue columns correspond to a system without hydrodynamic interactions and the red ones to a system with them.

From FIG. 4 we can observe that hydrodynamic interactions influence the assembly process. At the same instant of time and due to the fluid, the particles are more likely to form shorter chains compared with the case where we do not take into account hydrodynamic effects.

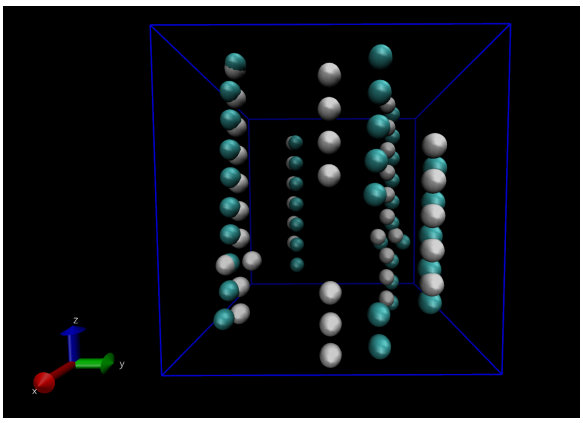

FIG. 5: Snapshot of the system. Grey particles are the representation of the system after 200 million time steps without taking into account hydrodynamic effects. Superposed , blue particles are the representation of the system at the same time point considering hydrodynamic effects.

Despite having the same initial configuration, the system evolves in different ways and as we can see from FIG. 5, the final state is different.

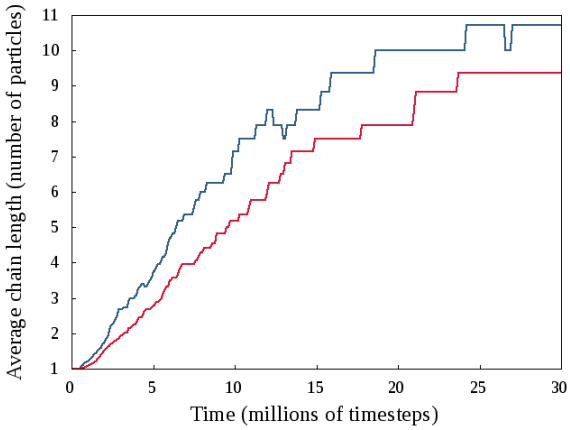

FIG. 6: Evolution of the chain average length according to the time step on a 150 particle system. The blue line corresponds to the system without considering hydrodynamic interactions and the red one is taking them into account.

We can appreciate from FIG. 6 that due to the hydrodynamics, the system has more difficulties in the assembly process compared to the case without hydrodynamic interactions. If we pay attention to a certain time step, at this point, the chain average length without hydrodynamic effects is larger that in the case where we contemplate these interactions. This phenomenon is at-

tributable to the fact that hydrodynamic interactions oppose the formation of aggregates.

C. Couette flow

Finally let us consider the effect of a Couette flow in the $\hat{x}$ direction ($v_x = \gamma z$, where γ is a constant) in the aggregation process. This flux gives more velocity to the particles that have a higher z coordinate and assuming that there is a wall at Z=0, we must take into account the steric interaction of the particles with the wall and the effect of the hydrodynamic interactions in its presence which behaviour is implemented through the Blake tensor as mentioned in the previous section.

So now we have the same interactions as before when it comes to the assembly process, but on the other hand the speed difference of particles at different high altitudes will cause a tendency to separate them.

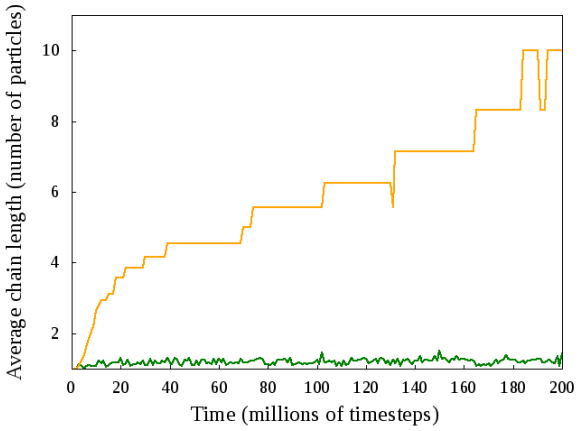

FIG. 7: Evolution of the chain average length according to the time step on a 50 particle system under the influence of a Couette flow. The green line corresponds to a $\gamma = 10^{-1}\ t_0^{-1}$ and the orange line to a $\gamma = 10^{-3}\ t_0^{-1}$.

At this point we have two possible scenarios. If the attractive force is greater than the force due to the Couette flow, the chain formation will be possible. Otherwise, if magnetic force is not able to counter the flow, the assembly process will not take place.

Considering that the particles forming chains are in contact ($z_1 - z_2 = 2R$) and oriented in the z-direction, we can find the γ value in which the difference of forces upon the particles due to the flow equals the magnetic force between them ($\gamma*$).

$$12\pi\eta R^2\gamma* = \frac{3\mu_0}{2\pi(2R)^4}m^2 \tag{10}$$

From where we obtain $\gamma* \simeq 4421\ s^{-1} = 0.037\ t_0^{-1}$. Where t_0 is the unit of time on our system units.

If we bring into comparison values of γ such that $\gamma \gg \gamma*$ or $\gamma \ll \gamma*$ we will be able to see, as in FIG.7, that in the case with $\gamma \gg \gamma*$ the system particles are not able to assemble into chains, corresponding to the case in which the shear caused by the flow beats the magnetic force .On the other hand when $\gamma \ll \gamma*$ we can clearly see aggregation between particles.

Notice from Eq.(10) that $\gamma* \sim \frac{m^2}{R^6}$, but we have to keep in mind that $m \sim R^3$ due to its dependence with the particle volume. Therefore, $m \sim \frac{R^6}{R^6}$ obtaining as a result that $\gamma*$ does not depend on the particle radius.

V. CONCLUSIONS

We have studied the influence of hydrodynamics in the formation of superparamagnetic particle chains under the influence of an external magnetic field through molecular dynamic simulations. We have observed that hydrodynamic interactions have an effect on the aggregation of these particles, slowing down the assembly process.

We have also analysed the effect of an external Couette flow on the formation of aggregates, observing that according to the shear value of this flow, the system is capable to form chains or not. A possible use of this knowledge is to control the assembly processes if we can regulate the system flow.

Acknowledgments

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